

ELECTRICAL CHARACTERIZATION OF $\beta \rightarrow \alpha$ -Sn TRANSITION IN HIGH TIN CONTENT SOLDER ALLOYS WITH DIFFERENT INOCULATORS

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Abstract. The identification of allotropic transition of the metallic β -Sn to non-metallic α -Sn in Sn-rich solders joints is crucial for electronics working in sub-zero temperatures. This phenomenon was characterized by electrical resistance measurements in SnCu1 and Sn99Ag0.3Cu0.7 alloys inoculated with InSb, CdTe and α -Sn. Samples were stored at -18°C for 10 weeks. The transition showed characteristic differences at the different alloys and inoculators, like different nucleation, growth and the saturation stages. Although the presence of α -Sn initiates the transition faster than the other inoculators, but the higher diffusion rate of the non-tin inoculators results in much more serious destruction of the samples. The results of the electrical resistance measurements were validated with metallurgical cross-sections.

Keywords: Tin pest, electrical resistance, allotropic transition, solder alloy, inoculator

1. Introduction

In microelectronics tin (Sn) is the base material of the solder alloys and surface finish. Sn has two main allotropes, the metallic β -Sn (applied in microelectronics) and the brittle and semiconductor α -Sn. β Sn is stable between 13.2 °C and 231.9 °C and α -Sn is stable below 13.2 °C. The “tin pest” is a spontaneous allotropic transition of β -Sn to α -Sn below 13.2 °C. The transition has 3 phases: nucleation, growth and saturation [1]. The signs of the transition is the occurrence of discolored spots which later change into characteristic warts. The transition causes volume increase, which can lead to the deterioration of the samples [2]. Tin pest is an autocatalytic reaction, the appearance of α -Sn speeds up the transition [3]. Tin pest can occur in high tin content alloys as well [1, 3] which are used in the microelectronics. Some soluble elements in Sn can suppresses the transition (like Pb, Bi, Sb) some has the opposite effect (like Cd, Au) [4]. The transition is slow (can takes years) due to a high activation energy. However, the nucleation time can be reduced with the application of inoculators such as CdTe or InSb (with the same crystallographic

parameters to the α -Sn) or α -Sn itself [3]. Tin pest can be investigated with electrical resistance measurements [5], since the transition from conductor to semiconductor properties and the mechanical deterioration changes the electrical resistance of the samples. In this work, the α -Sn transition was characterized by electrical resistance measurements in the case of different solder alloys with different inoculator materials.

2. Materials and Equipment

Sn99Cu1 and Sn99Ag0.3Cu0.7 solder alloys were investigated. Samples were prepared with the size: 45x6x3 mm³ (Fig 1a). Three different inoculator powders were applied: α -Sn, InSb and CdTe, which was pressed onto the lateral surfaces of the samples by a mechanic laminator with 30kN force. Before inoculation, the samples were cleaned in HCl solution to remove the oxide which could disturb the process. 15 samples were prepared from each sample types and they were stored at -18 °C for 10 weeks. The electrical resistance was measured by 4-wire method with an AGILENT 4338B milliohmmeter. The measurement accuracy of the instrument at the m Ω range is under 3 % and the repeatability error is under 2%. The initial resistance values of the samples were $0.25 \pm 0.015 \text{ m}\Omega$. Cross-sections were also analysed by an Olympus BX51 metal microscope to compare the resistance changes with the amounts of transformed Sn.

3. Results and Discussion

On the Sn99Cu1 samples inoculated with InSb, the warts of α -Sn appeared after 2 weeks (Fig 1b). After 3 weeks of nucleation, all of the samples showed 5–20 % of resistance increase and in the growth phase (3–6 weeks) considerable increase of electrical resistance was occurred (Fig. 2a). The maximum was ~33 times (to 8.3m Ω). The deviation was very high due to the combined effect of the not even inoculation and the autocatalytic nature of the transition. After 6 weeks, the electrical resistance increase reached the saturation phase. Skwarek et al. proved by Mössbauer spectroscopy as well, that the transition significantly slow down after the rapid growth phase [6]. After 8-9 weeks, the samples started to deteriorate into powder (Fig. 1c).

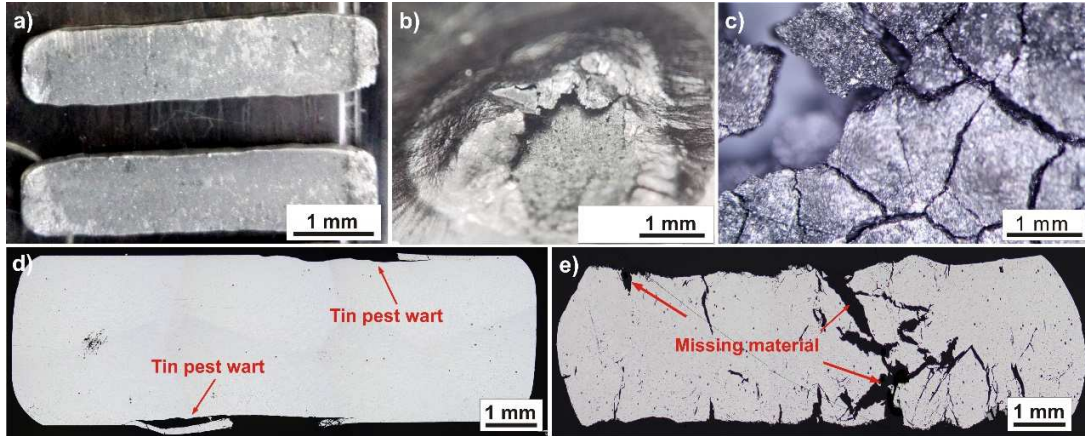


FIGURE 1. The α -Sn transition: a) the samples b) tin pest warts [6], c) deterioration of the sample; d) Cross-sections of Sn99Cu1 samples inoculated with α -Sn; e) Cross-sections of Sn99Cu1 sample inoculated with InSb.

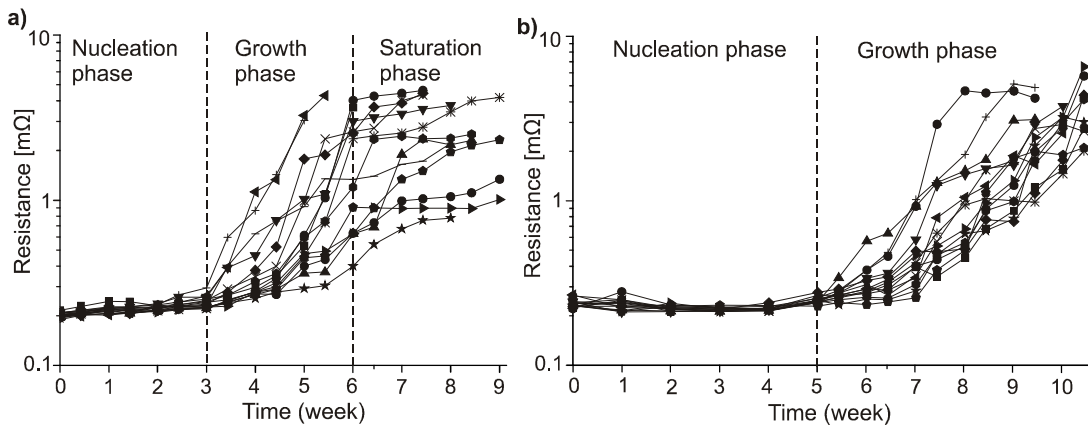


FIGURE 2. Electrical resistance change of Sn99Cu1 samples a) inoculated with InSb, b) inoculated with CdTe.

On the Sn99Cu1 samples inoculated with CdTe, the nucleation phase was much longer, the first tin pest warts appeared only after 4 weeks and the resistance increase started only after 5 weeks (Fig 2b). The maximum was ~ 34 times (to $8.58\text{m}\Omega$). Here the saturation phase was not found, like in the research of Di Maio and Hunt, who neither found saturation phases at SnCu and SnAg alloys inoculated with CdTe [1]. After 9-10 weeks the samples started to deteriorate. The samples from Sn99Ag0.3Cu0.7 inoculated with InSb and CdTe were persistent against tin pest. In the case of α -Sn inoculator both of the alloys showed similar behaviour: the first tin pest warts already appeared after some days and the nucleation phase was only 2 weeks. However, only a minor electrical resistance increase occurred still the 5th week (10-15%),

where it was saturated and the deterioration of the samples was not observed at all. Cross-sections were prepared in order to understand the different electrical behaviour of the samples. Sn99Cu1+InSb sample (resistance changed 4 times in 4 weeks) compared with Sn99Cu1+ α -Sn sample (resistance changed only 1.15 times in 8 weeks). In the case of α -Sn inoculation, only the typical lateral tin pest warts were found on the surface of the samples (“layer like” separations (Fig 1d). While in the case of InSb, intense vertical expansion were found (Fig. 1e) which caused the deterioration of the samples. This explains the minor resistance increase at α -Sn inoculator as well as the very high resistance increase at the InSn and CdTe inoculators. This effect is probably the result of the diffusion of the InSn and CdTe inoculators into the sample body and induction of the α -Sn transition inside the sample body as well.

4. Conclusion

The Sn99Cu1 alloy showed more susceptibility for α -Sn transition than the Sn99Ag0.3Cu0.7 alloy which showed the transition only in the case of α -Sn inoculation. InSb inoculator initiated the tin pest phenomenon with shorter nucleation time than CdTe, but finally very high electrical resistance increase and deterioration of the samples occurred with both inoculators. In the case of InSb inoculator the α -Sn transition reached the saturation phase, while with CdTe it did not. The intense vertical expansion of the tin pest with InSb and CdTe inoculators, probably due to their diffusion in the sample body. Consequently, the effect of the inoculators on the nature of α -Sn transition has to be investigated further.

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